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(54) Titre : ADJUVANTS TECHNOLOGIQUES POUR LE TRAITEMENT DE COMPOSITIONS DE POLYMERES
SYNTHETIQUES

(54) Title: PROCESSING AIDS FOR THE PROCESSING OF SYNTHETIC POLYMER COMPOSITIONS

(57) Abrégé/Abstract:

The present invention relates to processing aids for the processing of synthetic polymer compositions based on carboxylic esters, where the processing aids are composed of, or comprise, partial esters which contain at least 18 carbon atoms, have a number-average molecular weight of from 300 to 10 000, and can be prepared by the reaction of saturated or unsaturated aliphatic and/or cycloaliphatic polycarboxylic acids or anhydrides of these with saturated or unsaturated aliphatic, cycloaliphatic and/or aromatic monoepoxides and/or monoalcohols optionally containing ether groups, where at least 10% and not more than 90% of the carboxyl groups of the polycarboxylic acids have been reacted and the polycarboxylic acids and anhydrides of these contain from 8 to 100 carbon atoms. The invention further relates to the use of these processing aids in synthetic polymer compositions, and also to synthetic polymer compositions which comprise these processing aids.



Processing aids for the processing of synthetic polymer compositions

This invention relates to processing aids for the processing of synthetic polymer compositions based on carboxylic esters, for improving surface quality, such as smoothness and gloss, surface-coatability, and the homogeneity of pigmented and/or filled synthetic polymer compositions. Alongside these properties, the processing aids of the invention have a stabilizing effect on mixtures of incompatible polymers, and improve the flow properties of these synthetic polymer compositions.

Processing aids (process auxiliaries) are needed only in relatively small amounts, but are important additives without which some synthetic polymers would be difficult to process and certain shaping processes would be impossible to carry out. They are used for most thermoplastic synthetic polymers and thermosets (curable moulding compositions), and have a decisive role in raising the output performance of production machinery, improving the quality of finished products, and permitting the use of new processing technologies.

Processing aids are used to improve flow behaviour and flowability of synthetic polymers, to improve homogeneity and stability of filled and unfilled synthetic polymer mixtures and synthetic polymer melts, to improve surface quality, and to reduce the adhesion of the melts or mixtures to machinery components, and for the resultant improvement in mould-release properties.

The requirements placed upon processing aids when used together with synthetic polymers are generally the following:

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- There must be no impairment of the underlying physical properties of the polymers, but there has to be the desired effect on the application-related properties of the finished components. Examples of these properties are surface smoothness, gloss, transparency, printability, weldability, tack, and also slip behaviour and blocking behaviour.

- There must certainly be no increase in the adhesion of synthetic polymer compositions and synthetic polymer melts to machinery components or tooling components, or in the resultant decomposition of the polymer. It is desirable that processing aids have antiadhesive properties.

- It should be possible to optimize the rheological behaviour of the synthetic polymers - from powder feed through to melt - and of the compounded synthetic polymer material, in order to obtain homogeneous plastified synthetic polymer melts and/or homogeneous compounded synthetic polymer materials.

20

An example of an overview of processing aids and their possible applications is found in:

Hans Batzer, Polymere Werkstoffe, Band II - Technologie 1 [Polymeric materials, volume II - Technology 1], Georg Thieme Verlag Stuttgart, 1984, pp. 328 et seq.,
Gächter/Müller, Kunststoff-Additive [Plastics additives], 3rd edition, Carl Hanser-Verlag, 1989, pp. 441-502.

30

Table 1: Processing aids and their uses:

Class of compound	Uses
Hydrocarbons, e.g. paraffin oil - polyethylene waxes	Lubricants and release agents for unplasticized and plasticized PVC, PS, PA and UP 0.1-1.0%, e.g.: higher surface gloss, e.g. in PE

	Amount used up to 5%
Alcohols, e.g. palmityl, stearyl, tallow fatty alcohol	Extrusion, injection moulding, calander - of unplasticized and plasticized PVC (Amount: 0.5-1.0%) Improvement in flowability, internal lubricant action, good compatibility, transparency
Ketones, e.g. stearone	Blown PO films as slip agent, reduced adhesion of films to machinery rollers
Carboxylic acids, e.g. stearic acids, oxidized polyethylene waxes	Processing of unplasticized and plasticized PVC, PS, CA, MF, and compounded rubber materials
Metal salts of carboxylic acids, e.g. Ca, Zn stearates	Processing of plasticized PVC, PO, PS, ABS, PF and MF. A different lubricant action depending on type, effect on melting behaviour of PVC, often used as costabilizers
Carboxamides, e.g. fatty acid monoamides, fatty acid diamides	Slip agents; antiblocking agent for PO Lubricant, slip agent in PVC, PS, PO processing
Carboxylic esters, e.g. fatty acid esters, esters of polycarboxylic acids	Lubricant for unplasticized and plasticized PVC, PS, PA and MF, processing aid for extrusion, calandering, blow moulding and vacuum moulding of PVC

The abbreviations used in the table have the following meanings:

- 5 PVC = Polyvinyl chloride
 PS = Polystyrene
 CA = Cellulose acetate
 MF = Melamine-formaldehyde resin
 PO = Polyolefin
 10 ABS = Acrylonitrile-butadiene-styrene copolymer
 PF = Phenol-formaldehyde resin
 PA = Polyamide
 UP = Unsaturated polyester resin
 PE = Polyethylene

15

Although a wide variety of processing aids have been described, problems constantly continue to arise in the

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use of these substances in the various synthetic polymer compositions.

It is widely known that some processing aids migrate at room temperature to the surface of finished components and thus impair their appearance, or else lead to undesired emissions due to their volatility. For example, stearic acid can deposit on the surface of plasticized PVC as an undesired white deposit (bloom).

10 Refined hydrocarbons, which are used as lubricants in the production of impact-modified PVC, also deposit on the surface at room temperature and give the synthetic polymer a greasy and dull appearance. When metal salts are used, e.g. zinc stearate, particularly in hot-curing synthetic polymer compositions, problems arise since there can be emissions from the finished parts due to these metal salts. These metal salts also cause adhesion problems when the finished parts are painted. These adhesion problems necessitate the use of additional measures, e.g. alkali treatment (power wash), to improve surface-coatability of the finished component. This is an additional undesired operation which is also hazardous to the environment.

Effects also arise between processing aids and certain components, for example if their solubility limit is exceeded. This leads to "plate-out" when using certain dyes, pigments, stabilizers and fillers. This phenomenon occurs particularly when short-chain fatty esters are used.

30 Uses in polyolefin thermoplastics can result in interactions with light stabilizers, other stabilizers and antioxidants, possibly resulting in disruption of processing in the machinery and loss of stability in the finished products.

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US-A 4 210 571 and 4 210 572 describe coupling agents for the treatment of fillers for hot-curing resins based on carboxylic ester derivatives of mono-, di- and trihydroxy fatty acid esters of mono- or polyhydric
5 alcohols having from 1 to 4 carbon atoms, and use of these. These coupling agents create adhesion between the filler and the resin. No use as processing aids is described.

10 EP 0 22 977 B1 (DE 36 50 587 T2, US 4,622,354) describes the preparation of a curable, phase-stabilized polyester moulding composition. A problem with many curable moulding compositions, e.g. with polyester resins, is that the individual constituents
15 of the polyester resin are mutually immiscible. During processing, therefore, the components tend towards phase separation. According to the abovementioned patent, the use of fatty acids having from 5 to 28 carbon atoms reduces the tendency towards phase
20 separation. A disadvantage here is that the fatty acids described react with the additive MgO and therefore deprive this additive of its effective use (adjustment of final processing viscosity).

US-A 4 172 059 describes a curable moulding composition
25 made from an unsaturated polyester resin or from a terminally unsaturated vinyl ester resin, and also describes mixtures of the two components with an olefinically unsaturated copolymerizable monomer, with a thickener, and with a filler, and also at least 0.4%
30 by weight of a viscosity-lowering processing aid. This viscosity-lowering processing aid is composed of an aliphatic monocarboxylic acid having at least 6 carbon atoms in the chain.

Here again, a disadvantage is that the monocarboxylic
35 acids described react with the additive (MgO), as described above.

In the light of the problem that although there is a wide variety of processing aids on the market there are no substances which favourably affect the surface
5 quality of synthetic polymer compositions, advantageously affect the flow properties of synthetic polymer compositions both during preparation and during processing, and also improve parameters such as surface-coatability and homogeneity, the object was to
10 find processing aids which do not exhibit the weaknesses listed.

A further object, in the light of more stringent environmental requirements in relation to minimum migration tendency and emission tendency, was to find
15 processing aids which fulfil all of the abovementioned requirements and do not lead to migration phenomena and emission phenomena (fogging, bloom) in the final application.

20 Surprisingly, the object set has been found to be achieved by using partial esters.

The present invention therefore provides processing aids for the processing of synthetic polymer
25 compositions based on carboxylic esters, characterized in that they are composed of, or comprise, partial esters which contain at least 18 carbon atoms, have a number-average molecular weight of from 300 to 10 000, and can be prepared by the reaction of saturated or
30 unsaturated aliphatic and/or cycloaliphatic polycarboxylic acids or anhydrides of these with saturated or unsaturated aliphatic, cycloaliphatic and/or aromatic monoepoxides and/or monoalcohols optionally containing ether groups, where at least 10%
35 and not more than 90% of the carboxyl groups of the polycarboxylic acids have been reacted and the

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polycarboxylic acids and anhydrides of these contain from 8 to 100 carbon atoms.

It is preferable for from 20 to 70%, particularly from
5 25-60%, of the carboxyl groups of the polycarboxylic acids to have been esterified.

Preference is given to polycarboxylic acids which contain from 2 to 4 carboxylic acid groups.

10

Very particularly preferred polycarboxylic acids are the dimer or trimer acids having from 30 to 60 carbon atoms and obtainable by polymerization of unsaturated fatty acids.

15

The acid value of the partial esters is preferably at least 10 mg KOH/g.

The invention also provides the use of the processing
20 aids in the processing of synthetic polymer compositions.

The partial esters of the invention may be used either in thermoplastic synthetic polymer compositions or else
25 in thermoset synthetic polymer compositions, as in DIN 7724.

Within thermoplastic synthetic polymer compositions, one preferred use of the partial esters is use in
30 polyolefins (e.g.: polypropylene, polyethylene), in ethylene-vinyl acetate copolymers, in polyamides, in polycarbonates, in polystyrenes, in polyethylene terephthalates, in polyesters, in poly(meth)acrylates, or in mixtures of these.

35

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One particularly preferred field of use of the partial esters is their use in PVC, in particular soft PVC and paste PVC.

5 Within thermoset synthetic polymer compositions, one preferred use of the partial esters is use in curable (meth)acrylate resins and mixtures of these. Preferred (meth)acrylate resins in this context are polymer compositions which are produced by bulk polymerization
10 during the casting procedure. Prepolymerization takes place first here up to conversion of from 10 to 30% of polymer, at the boiling point of the monomer. The resultant syrup (PMMA is soluble in the monomer) is then polymerized in cells with movable cell walls, in a
15 water bath (cell-casting process).

Another preferred use is use of the partial esters in polyurethane systems (PU systems). Among the various structural types of PU, it is the crosslinked polyether polyurethanes and crosslinked polyester polyurethanes
20 which are relevant here.

A very particularly preferred field of use of the partial esters is their use in unsaturated polyester resin systems (UP). These are solutions of unsaturated
25 polyesters in a vinyl monomer, mostly styrene. They are cured by crosslinking copolymerization of the vinyl monomer with the polymerizable double bonds of the polyester. Accelerated resins have the accelerator required for cold curing previously added.

30 Very particularly preferred applications of the partial esters in UPs are

UP moulding compositions, in particular SMC, BMC, DMC, TMC, LDMC.

The term SMC describes fibre-reinforced moulding
35 compounds in sheet form (Sheet Moulding Compounds).

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The term BMC describes dry, indeed in part flowable, pellets (Bulk Moulding Compounds).

The term DMC describes dough-like moulding compounds (Dough Moulding Compounds).

- 5 The term TMC describes thickened moulding compounds (Thick Moulding Compounds).

The term LDMC describes fibre-reinforced moulding compounds of low density (Low Density Moulding Compounds).

10

In the case of SMC moulding compounds, the partial esters of the invention may be used either in LS (Low Shrink) or LP (Low Profile) systems.

- 15 LP systems are compounded materials which give substantial compensation of shrinkage. LS systems do not achieve the shrinkage compensation of LP resins, but are substantially easier to colour.

- 20 The abovementioned synthetic polymer compositions may be processed by injection, compression, blow moulding (extrusion blow moulding, injection blow moulding), extrusion, coating/spreading, casting, calendering (rolled melt processes), impregnation, pultrusion or
25 foaming.

- In processing the abovementioned synthetic polymer compositions, use may be made of fillers and reinforcing agents, e.g. chalk (CaCO_3) - natural or
30 synthetic, alumina trihydrate (ATH), kaolin, talc, feldspar, metal oxides, powdered quartz, rock flour, wollastonite, mica, glass fibres, glass beads; synthetic organic substances (e.g. synthetic fibres, polyesters, polyamides, aramids), carbon fibres (C
35 fibres); naturally occurring organic substances (e.g. wood flour, cellulose).

- 10 -

The invention also provides synthetic polymer compositions which comprise from 0.05 to 10% by weight of the processing aids of the invention, and also, where appropriate, comprise the abovementioned fillers and auxiliaries.

Various thermoplastic synthetic polymer compositions of the invention will first be described by way of example below, followed by various thermoset synthetic polymer compositions of the invention.

Calandering compositions (synthetic polymer compositions for calandering)

Thermoplastics which have a distinct plastic region with high melt viscosity (about 10^2 - 10^3 Pa·s) can be processed by calandering. Examples of processes for this purpose are described in Polymere Werkstoffe- Band III, Technologie 2 [Polymeric materials, Volume III, Technology 2], by Hans Batzer, Georg Thieme Verlag, Stuttgart, 1984 edition, pp. 251 et seq. Examples of products produced in this way are floorcoverings, films with a very wide variety of uses made from unplasticized, semirigid, or plasticized PVC.

25

In order to prevent the melt from adhering to the metal surfaces, internal lubricants are often added, e.g. fatty alcohol esters of long-chain fatty acids (C_{14} - C_{18}). They improve melt flow by reducing the friction between the PVC particles. External lubricants, e.g. paraffins and waxes, are also added in order to ease separation of the calandering composition from the rolls. Downstream of the calander there is often printing machinery or embossing calanders (e.g. to produce decorative films, upholstery films or synthetic-leather films from plasticized PVC). This

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further processing makes it advisable to replace the internal and external lubricants used hitherto by the partial ester of the invention, in order thereby to utilize the advantages of better surface-coatability or printability.

The internal and external lubricants are simply replaced here by the processing aid of the invention during the mixing or dispersion process.

10 Injection-moulding compositions

Moulding compositions made from thermoplastic synthetic polymers are mainly termed injection-moulding compositions. The moulding compositions are composed of polymeric base material and of additives, e.g. fillers or reinforcing materials. Injection-moulding compositions often use polymers with lower molar masses than those used in extrusion compositions, and they therefore have more favourable melt viscosity and flowability. However, when use is made of additives, e.g. flow promoters and lubricants, the action of these always has to be taken into account. Any reduction in the relative molar mass of the polymer impairs mechanical properties, and lubricant additives also lower softening point, for example.

Further detailed descriptions of additives in injection-moulding compositions, and the processing and composition of these, are found in Polymere Werkstoffe-Band III, Technologie 2 [Polymeric materials, Volume III, Technology 2], by Hans Batzer, Georg Thieme Verlag, Stuttgart, 1984 edition, pp. 204-221. Here again, it has proven to be advisable, particularly in the processing of unplasticized PVC, to use the partial esters of the invention to replace the internal and external lubricants used hitherto, in order thereby to utilize the advantages of better surface-coatability or printability.

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To this end, the internal and external lubricants are simply replaced by the processing aid of the invention during the mixing or dispersion process. Here again, improved surface quality is apparent with respect to smoothness and gloss, as is an additional effect in homogenization during the colouring process. This effect is particularly advantageous for uses where surface-coating is not intended.

10

Extrusion compositions

Extrusion compositions often use polymers with higher molar masses than those used for injection-moulding compositions, e.g. with higher melt viscosity and lower flowability. The higher melt viscosity of the extrusion compositions improves strength between discharge from the die and the calibrator. The higher relative molar mass and therefore higher melt viscosity is also associated with better mechanical properties, but with greater difficulty in processing by injection moulding. A detailed description is found in Polymere Werkstoffe-Band III, Technologie 2 [Polymeric materials, Volume III, Technology 2], by Hans Batzer, Georg Thieme Verlag, Stuttgart, 1984 edition, pp. 244 et seq.

Here again, it has proven advisable, especially when processing PVC profiles and PVC for outdoor use, to use the partial esters of the invention to replace the internal and external lubricants used hitherto, in order thereby to utilize the advantages of better surface-coatability or printability.

To this end, the internal and external lubricants are simply replaced by the processing aid of the invention during the mixing or dispersion process. Here again, better surface quality with respect to smoothness and gloss is apparent, as is an additional effect in homogenization during the colouring process. This

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effect is particularly advantageous for uses where no surface-coating is intended.

Examples which may be mentioned are window profiles,
5 the composition of which is as follows:

PVC, additives which increase impact strength, stabilizers, phosphite, epoxidized soya oil, 12-hydroxystearic acid, stearyl stearate, antioxidant, titanium dioxide, fillers (e.g. CaCO_3).

10

Coating compositions

According to DIN 8580, coating is a manufacturing process for applying an adherent layer made from a shapeless substance to a workpiece or substrate web.

15 The coating compositions mostly used are thermoplastics or - to a small extent - elastomers. Among the thermoplastics, PVC pastes are the most important. Among PVC pastes, a distinction is made between plastisols, which are mostly used, and organosols, the
20 latter not being relevant here.

Coating compositions are prepared by stirring pulverulent PVC paste grades (mostly based on emulsion PVC, also occasionally on suspension PVC) and additives (stabilizers), pigments and fillers into plasticizers,
25 by mixing or dispersion in appropriate assemblies.

A detailed description of the preparation process is found in Polymere Werkstoffe- Band III, Technologie 2 [Polymeric materials, Volume III, Technology 2], by Hans Batzer, Georg Thieme Verlag, Stuttgart, 1984
30 edition, pp. 254 et seq.

The floor coverings and synthetic leather coatings thus produced are often further processed via further surface treatment, e.g. embossing of a particular design, with the aid of embossing rolls, and/or
35 surface-coating by planography or gravure printing.

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This further processing makes it advisable to replace the internal and external lubricants used hitherto by the partial ester of the invention, in order thereby to utilize the advantages of better surface-coatability or printability.

To this end, the internal and external lubricants are simply replaced by the processing aid of the invention during the mixing or dispersion process.

Here again, better surface quality with respect to smoothness and gloss is apparent, as is an additional effect in homogenization during the colouring process using pigments. This effect is particularly advantageous for uses where no surface-coating is intended.

When embossing papers (e.g. imitation leathers) are used in the transfer process, it has proven advantageous to use the partial ester of the invention since there is a marked increase in the usage cycle of these embossing papers, which are mostly very expensive.

Various inventive and comparative formulations from the field of plastisol formulations for plasticized PVC are listed in the Examples section under Application examples - Application Example 1.

Thermosets (moulding compounds)

Moulding compounds generally comprise the following substances:

reactive resins, curing agents, optionally accelerators (this mixture often also being termed binder matrix) fillers and/or reinforcing materials, lubricants and release agents, pigments and/or dyes, other additives, e.g. stabilizers, flexibilizers, curing retarders and non-reactive resins.

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The fillers mainly used are chalk (CaCO_3), ATH, powdered quartz, rock flour, wollastonite, mica, and the reinforcing materials mainly used are glass fibres, synthetic organic substances (e.g. synthetic fibres, polyesters, polyamides, aramids), carbon fibres (C fibres); naturally occurring organic substances (e.g. wood flour and cellulose).

Details of the processing of these moulding compounds are given in Polymere Werkstoffe- Band III, Technologie 2 [Polymeric materials, Volume III, Technology 2], by Hans Batzer, Georg Thieme Verlag, Stuttgart, 1984 edition, pp. 224 et seq.

An example which may be mentioned is UP moulding compositions, in particular fibre-reinforced moulding compounds, as described in detail in Polymere Werkstoffe- Band III, Technologie 2 [Polymeric materials, Volume III, Technology 2], by Hans Batzer, Georg Thieme Verlag, Stuttgart, 1984 edition, pp. 235 et seq. These fibre-reinforced moulding compounds in sheet form (also termed Sheet Moulding Compounds or SMC) further divide into the groups LS (Low Shrink) and LP (Low Profile). LP systems are compounds which give substantial compensation of shrinkage. LS systems do not achieve the shrinkage compensation of LP resins but are substantially easier to colour. If SMC mouldings are intended for downstream surface-coating, e.g. in the case of bodywork components, preference is given to LP systems. Here again, the further processing has made it advisable to use the partial ester of the invention to replace the internal and external lubricants used hitherto, in order thereby to utilize the advantages of better surface-coatability or printability.

To this end, the internal and external lubricants are simply replaced by the processing aid of the invention during the mixing or dispersion process. Better

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stabilization of the compounds is also apparent, without any impairment of the shrinkage effect attributed to the LS and LP components. Here again, improved surface quality with respect to smoothness and gloss is apparent, as is an additional effect in homogenization during the colouring process. This effect is particularly advantageous for uses where no surface-coating is intended.

Various inventive and comparative formulations from the field of thermosets and SMC manufacture are listed in the Examples section under the heading Application examples - Application Example 2 and Application Example 3.

In order to illustrate the invention, the Examples section below demonstrates the preparation of various inventive and non-inventive processing aids and their suitability for applications.

Examples

Preparation examples

General preparation specification relating to the preparation examples listed in the table below

Components 1 and 2 are weighed, in the ratio given, into a suitable reaction vessel, and heated under nitrogen gas to about 80°C, with stirring. Component 3 is added, and the mixture is then heated to the temperature given under nitrogen gas. Any water of reaction produced is separated via a water separator. The progress of the reaction is checked by determining the acid value. Stirring is continued at the

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temperature given until the acid value given has been achieved. The mixture is then cooled and discharged.

The following substances, inter alia, were used:

- 5 • Pripol 1022 is a C36 dimer acid from Unichema
- Pripol 1009 is a hydrogenated C36 dimer acid from Unichema
- Pripol 1040 is a C54 trimer acid from Unichema
- 10 • The MA/fatty acid adduct from Example 17 is the product of an addition reaction of 1 mol of maleic anhydride onto a conjugated unsaturated C18 fatty acid mixture
- MPEG 350 is a methoxypolyethylene glycol with an average molar mass of 350 g/mol
- 15 • MPEG 500 is a methoxypolyethylene glycol with an average molar mass of 500 g/mol
- MPEG 750 is a methoxypolyethylene glycol with an average molar mass of 750 g/mol
- 20 • Polyglycol B11/50 is a butanol-started EO/PO polyether (EO:PO = 1:1) with an average molar mass of 1 020 g/mol
- Lutensol ON 50 is an oxo-alcohol-started EO polyether with an average molar mass of 400 g/mol

Preparation examples

Example	Component 1	Proportion by weight K1	Reacted acid groups in %	Component 2	Proportion by weight K2	Component 3	Proportion by weight K3	Reaction temperature [°C]	Acid value [mg KOH/g]
1	Pripol 1022	89.4	45	Butanol	10.1	p-Toluenesulphonic acid	0.5	190	94
2	Pripol 1022	72.3	40	Oleyl alcohol	26.7	Dodecylbenzenesulphonic acid	1	150	85
3	Pripol 1022	74.7	35	Stearyl alcohol	24.3	Dodecylbenzenesulphonic acid	1	150	94
4	Pripol 1022	72.7	30	MPEG 350	26.3	Dodecylbenzenesulphonic acid	1	180	99
5	Pripol 1022	82.5	15	Lutensol ON 50	17	p-Toluenesulphonic acid	0.5	180	136
6	Pripol 1022	91.4	20	2-Ethylhexanol	8.1	p-Toluenesulphonic acid	0.5	140	142
7	Pripol 1022	81	50	2-Ethylhexanol	18.5	p-Toluenesulphonic acid	0.5	140	78
8	Pripol 1022	73.3	80	2-Ethylhexanol	26.2	p-Toluenesulphonic acid	0.5	140	28
9*	Pripol 1022	68.7	100	2-Ethylhexanol	30.8	p-Toluenesulphonic acid	0.5	140	0
10	Pripol 1009	84.8	50	Hexenol	14.7	p-Toluenesulphonic acid	0.5	140	83
11	Pripol 1009	47.8	30	Polyglycol B11/50	51.2	Tetraisopropyl orthotitanate	1	180	66
12	Pripol 1040	74.9	25	Lutensol ON 50	24.4	p-Toluenesulphonic acid	0.7	180	104
13	Tetrapropenyl-succinic anhydride	49.9	50	Oleyl alcohol	49.9	p-Toluenesulphonic acid	0.2	120	105
14	Pripol 1009	73.8	20	MPEG 500	25.7	p-Toluenesulphonic acid	0.5	180	116
15	Pripol 1040	62.3	90	Isotridecyl alcohol	37.2	p-Toluenesulphonic acid	0.5	170	12
16	Pripol 1040	79.8	10	MPEG 750	19.5	p-Toluenesulphonic acid	0.7	180	133
17	MSA/fatty acid adduct	52.8	50	Oleyl alcohol	46.2	Dodecylbenzenesulphonic acid	1	170	97
18	Phthalic acid	54.9	25	Stearyl alcohol	44.6	Potassium carbonate	0.5	160	280
19	Trimellitic anhydride	44	30	Oleyl alcohol	55.3	Potassium carbonate	0.7	150	272
20	Pripol 1022	75.4	50	Ethylhexyl glycidyl ether	24.1	p-Toluenesulphonic acid	0.5	160	73

*: non-inventive comparative example

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APPLICATION EXAMPLES**Application Example 1**

- 5 The plastisol compositions given in the table below were prepared by homogenizing the constituents in the usual way in a mixer.

PLASTISOL FORMULATION FOR PLASTICIZED PVC

- 10 (Amounts given in parts by weight)

Application example	1a*	1b*	1c	1d*
DINP (Diisodecylphthalate)	275	275	275	275
Butyltin mercaptide, (Tinstab BTS 61 from Akzo Nobel)	2.5	2.5	2.5	2.5
Stabilizer preparation based on calcium/zinc carboxylate (Lankromark LZC 184 from Akzo Nobel)	5	5	5	5
TiO ₂ , rutile type (Kronos 2300 from Kronos)	100	100	100	100
Calcium carbonate (Calcilit 8G from Alpha Calcit)	285	285	285	285
Alkylphenol ethoxylate (Lankroplast V2023 from Akzo Nobel)	7.5	7.5	7.5	7.5
Isoparaffin fraction, bp 186-204°C (Isopar J from ExxonMobil)	50	50	50	50
Microsuspension PVC, K value 71 (Evipol MP 7151 from European Vinyl Corp.)	500	500	500	500
C36 dimer acid* (Pripol 1022 from Unichema)		5		
Preparation Example 7			5	
Preparation Example 9*				5
Results:				
Surface tension ¹⁾ [mN/m]	44.5	46.0	52.1	44.5
Demouldability ²⁾	very bad	good	very good	very bad
Yellowing	none	marked	slight	none

*: Non-inventive

- 15 Since wettability and adhesion during surface-coating are substantially dependent on the polarity of the substrate, the surface tension of formulations 1a-1d was determined.

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1)¹: To measure surface tension, the plastisols were fully gelled in a Mathis oven, using 200 µm wet layer thickness, at 200°C for 2 minutes. During this process, the non-inventive formulation 1b prepared using the unesterified dimer acid exhibited marked yellowing due to high carboxy group content, in contrast to the other specimens. Surface tension was measured using a Krüss G2 surface-tension tester. The reference/test liquids used here were water, glycerol, ethylene glycol, 1-octanol and n-dodecane.

Easily the highest surface tension and therefore best surface-coatability was found for inventive formulation 1c. In contrast to this, comparative formulations 1b and 1d using unesterified or fully esterified dicarboxylic acid showed no increase in surface tension or only a slight increase.

2)²: To test demouldability, the plastisols were spread on a gradient-oven steel sheet at a wet-layer thickness of 1 000 µm. A Shuller SH60/21 glass nonwoven was laid into the material. The nonwoven was impressed by a rubber roller. The sheets were then stoved in a gradient oven with a temperature gradient of from 180 to 220°C and with a stoving time of 2 minutes. Immediately after the stoving process, the glass nonwoven was pulled away from the sheet and an assessment was made of the residual amount of adherent PVC.

Application Example 2

THERMOSETS/CURABLE MOULDING COMPOUNDS - SMC MANUFACTURE

The SMC formulations given in the table below were prepared by first homogenizing all of the liquid constituents, using a dissolver, and then mixing to incorporate all of the solids.

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TEST SPECIFICATION ELECTRIC GREY - RAL 7032

Application example	2a*	2b*	2c	2d*	2e*	2f*	2g	2h*
Resin 1 Palapreg P17-02 Standard glycol-phthalic-acid resin (35% strength in styrene)	70.00	70.00	70.00	70.00	70.00	70.00	70.00	70.00
Resin 2 Palapreg H 814-01 Polystyrene (33% strength in styrene)	30.00	30.00	30.00	30.00	30.00	30.00	30.00	30.00
Pigment paste in monomer-free polyester resin, Brohl Chemie, Electric grey RAL 7032 - 65 L (a.V.)	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Tert-butyl peroxybenzoate Curing agent (Trigonox C from Akzo)	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
2,6-Di-tert-butyl-4-methylphenol Inhibitor (Ionol CP)	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Filler 1 Chalk (Millicarb OG)	50.00	50.00	50.00	50.00	50.00	50.00	50.00	50.00
Filler 2 Al(OH) ₃ (Martinal ON 921)	120.00	120.00	120.00	120.00	120.00	120.00	120.00	120.00
PE powder Coathylene HA 1681	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Luvatol MK 35 NV (35% strength MgO in monomer-free UP resin)	2.00	2.00	2.00	2.00	2.70	2.70	2.70	2.70
Zn stearate*	4.00				4.00			
C36 dimer acid (Pripol 1022 from Unichema)*		3.00				3.00		
Preparation Example 7			3.00				3.00	
Preparation Example 9*				3.00				3.00
Thickening behaviour results:								
Viscosity [Pa.s] after								
3 days of storage	120 000	70 000	110 000	120 000	150 000	75 000	150 000	150 000
5 days of storage	150 000	80 000	140 000	150 000	>160 000	100 000	>160 000	>160 000
8 days of storage	>160 000	90 000	>160 000	>160 000	>160 000	105 000	>160 000	>160 000

*: Non-inventive comparative examples

- 10 To test thickening behaviour, a Brookfield viscometer was used (DVII, TF spindle at 0.5 rpm) to measure the viscosity of the compounding materials prepared as in the table above after storage at 20°C. Measurements 2a, 2c and 2d exhibited a thickening performance which was
- 15 identical within the bounds of the usual technical

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variations, whereas formulation 2b prepared using the unesterified dicarboxylic acid exhibited marked impairment of thickening level.

The same picture results for formulations 2e-h prepared using an increased amount of MgO. This means that even an increase in the content of MgO cannot compensate the adverse effect of the unesterified dicarboxylic acid (see comparative formulation 2f).

SMC prepregs were produced using formulations 2a-d on a Schmidt and Heinzmann experimental SMC plant, by applying the resin composition between two polyamide substrate films. (Belt speed: 5.5 m/min; doctor gap: 1.6 mm; weight per unit area: 4 000 g/m²; glass grade used: OC RO7 4 800 tex from Owens Corning; glass content: 97 parts by weight, corresponding to 25% by weight, based on the entire formulation.)

For further processing after thickening was complete, the substrate films have to be capable of being peeled away entirely from the resin mats prior to the pressing procedure, and the prepregs themselves are to be as dry as possible and free from tack. Another assessment criterion used was the appearance of the peeled film which should be as transparent as possible and not have any adhesions of resin.

After storage for 5 days at room temperature, the thickened SMC prepregs were cut out to give pieces of 860 g, and the substrate film was peeled off, and its appearance evaluated.

Assessment of handlability of prepregs prior to pressing procedure

Formulation	Prepreg surface	Film appearance
2a*	dry, slightly tacky	very opaque with considerable adhesions

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		of compounded material
2b*	very tacky	very opaque with considerable adhesions of compounded material
2c	dry, not tacky	transparent, no adhesions of compounded material
2d*	very tacky	milky, with marked adhesions of compounded material

*: Non-inventive comparative examples

In the case of inventive formulation 2c, particularly easy and tack-free removal of the substrate film was possible without cobwebbing.

Testing of release action, colour homogeneity and surface quality after the moulding process

The SMC pieces freed from the substrate film were moulded to give test sheets, using 40% mould filling. The temperature used here was from 150 to 155°C, the moulding time was 180 s, and the ram pressure was 1 200 kN.

The finished moulded sheets were then visually assessed for colour homogeneity and surface quality.

To evaluate surface quality, the sheet to be tested was held slightly obliquely to the window, with a comparative sheet. The clarity with which the test surface could reflect objects was evaluated.

20

Formulation	Assessment of demoulding	Colour homogeneity	Surface quality
2a*	O.K.	poor, marked marbling	poor, matt
2b*	O.K.	poor, marked marbling	slightly better than 2a
2c	O.K.	slight marbling, best homogeneity	glossy
2d*	poor, cracks in sheets	Assessment impossible, since marked surface disruption by matt effects/adhesions/cracks	

*: Non-inventive comparative examples

The test sheets produced using the comparative formulations 2a and 2b exhibited poor colour homogeneity, and the glass fibre structures which were clearly recognizable here caused marked marbling

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effects. In addition, the surface was matt. In contrast, the test sheets produced using inventive formulation 2c gave a visual impression which was overall markedly improved and resulted from a smoother, more glossy surface and better colour homogeneity, with markedly fewer marbling effects.

Test for surface-coatability

The SMC sheets were surface-coated using a commercially available 2-component automotive repair coating based on acrylic resin/isocyanate.

Weight ratio of surface coating to curing agent = 2:1

Mixing specification for surface coating:

Spies Hecker - Permacron surface coating for mixing,
Series 257 AG201 white (= stock surface coating)
Spies Hecker - Permacron MS Härter plus 3040 kurz
2 parts by weight of stock surface coating: 1 part by weight of curing agent

The SMC sheets were surface-coated, using a layer thickness (dry) of from 45 to 50 μm , and after air-drying they were stored at 80°C for about 24 h. The sheets were then subjected to a cross-cut test to test adhesion. (Evaluation scale from Gt0 to Gt5: Gt0 = good adhesion of surface coating, Gt5 = poor adhesion of surface coating)

Results of adhesion test

Formulation	Cross-cut
2a*	Gt5
2b*	Gt4
2c	Gt1
2d*	NOT TESTED

*: Non-inventive comparative examples

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The test sheets produced using inventive formulation 2c exhibited substantially better adhesion of surface coating when compared with comparative formulations 2a

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and 2b. No testing of surface-coatability of the sheets of comparative formulation 2d could be carried out, since the surface quality was too poor, due to defective demoulding.

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Application Example 3

The test mixing specification used was as in Application Example 2, but instead of electric grey
10 RAL 7032 pigment paste, use was made of a cobalt blue pigment paste from Freilacke, Emil Frei GmbH & Co. Lackfabrik, Durelastik Farbpaste, VP BÜ 1232.
Here again, easily the best surface quality and
homogeneity was achieved when using the inventive
15 formulation.

Patent Claims

1. Processing aids for the processing of synthetic polymer compositions based on carboxylic
5 esters, characterized in that they are composed of, or
comprise, partial esters which contain at least 18
carbon atoms, have a number-average molecular weight of
from 300 to 10 000, and can be prepared by the reaction
of saturated or unsaturated aliphatic and/or
10 cycloaliphatic polycarboxylic acids or anhydrides of
these with saturated or unsaturated aliphatic,
cycloaliphatic and/or aromatic monoepoxides and/or
monoalcohols optionally containing ether groups, where
at least 10% and not more than 90% of the carboxyl
15 groups of the polycarboxylic acids have been reacted
and the polycarboxylic acids and anhydrides of these
contain from 8 to 100 carbon atoms.
2. Processing aids according to Claim 1,
20 characterized in that the polycarboxylic acids contain
from 2 to 4 carboxylic acid groups.
3. Processing aids according to Claim 1 or 2,
characterized in that the polycarboxylic acids are
25 dimer or trimer acids having from 30 to 60 carbon atoms
and obtainable by polymerization of unsaturated fatty
acids.
4. Processing aids according to any of Claims 1
30 to 3, characterized in that the partial esters have an
acid value of at least 10 mg KOH/g.
5. Use of the processing aids according to any
of Claims 1 to 4 in the processing of synthetic polymer
35 compositions.

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6. Use of the processing aids according to any of Claims 1 to 4 in the processing of thermoplastic synthetic polymer compositions.

7. Use according to Claim 6 in the processing of
5 synthetic polymer compositions based on polyvinyl chloride, on polyvinylidene chloride, on polyethylene, on polypropylene, on polyamide, on polycarbonate, on polystyrene, on poly(meth)acrylate, on polyester, on ethylene-vinyl acetate copolymers, on polyacrylo-
10 nitrile, on graft polymers of vinyl chloride and vinyl acetate, on copolymers of vinyl chloride and vinyl acetate, or mixtures of the stated thermoplastics.

8. Use according to Claim 7, characterized in
15 that the synthetic polymer compositions are based on soft PVC or on paste PVC.

9. Use of the processing aids according to any of Claims 1 to 4 in the processing of thermoset
20 synthetic polymer compositions.

10. Use according to Claim 9, characterized in that these are unsaturated polyester resin systems, polyurethane systems, curable (meth)acrylate resin
25 systems, or mixtures of these.

11. Use according to Claim 10, characterized in that the unsaturated polyester resin systems are unsaturated polyester resin system moulding
30 compositions.

12. Use according to Claim 11, characterized in that the moulding compositions are sheet moulding compounds, bulk moulding compounds, dough moulding
35 compounds or thick moulding compounds.

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13. Use according to any of Claims 5 to 12 in the processing of synthetic polymer compositions by injection, compression, extrusion, coating, casting, calendering, impregnation, foaming or pultrusion.

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14. Synthetic polymer compositions comprising from 0.05 to 10% by weight of the processing aids according to any of Claims 1 to 4.

10 15. Synthetic polymer compositions according to Claim 14, characterized in that they also comprise fillers, heat stabilizers, light stabilizers, antistats, flame retardants, reinforcing materials, pigments and/or dyes, processing auxiliaries,
15 lubricants and release agents, impact modifiers, antioxidants, blowing agents or optical brighteners.

Abstract

The present invention relates to processing aids for the
5 processing of synthetic polymer compositions based on
carboxylic esters, where the processing aids are composed of,
or comprise, partial esters which contain at least 18 carbon
atoms, have a number-average molecular weight of from 300 to
10 000, and can be prepared by the reaction of saturated or
unsaturated aliphatic and/or cycloaliphatic polycarboxylic
10 acids or anhydrides of these with saturated or unsaturated
aliphatic, cycloaliphatic and/or aromatic monoepoxides and/or
monoalcohols optionally containing ether groups, where at least
10% and not more than 90% of the carboxyl groups of the
15 polycarboxylic acids have been reacted and the polycarboxylic
acids and anhydrides of these contain from 8 to 100 carbon
atoms. The invention further relates to the use of these
processing aids in synthetic polymer compositions, and also to
synthetic polymer compositions which comprise these processing
20 aids.
